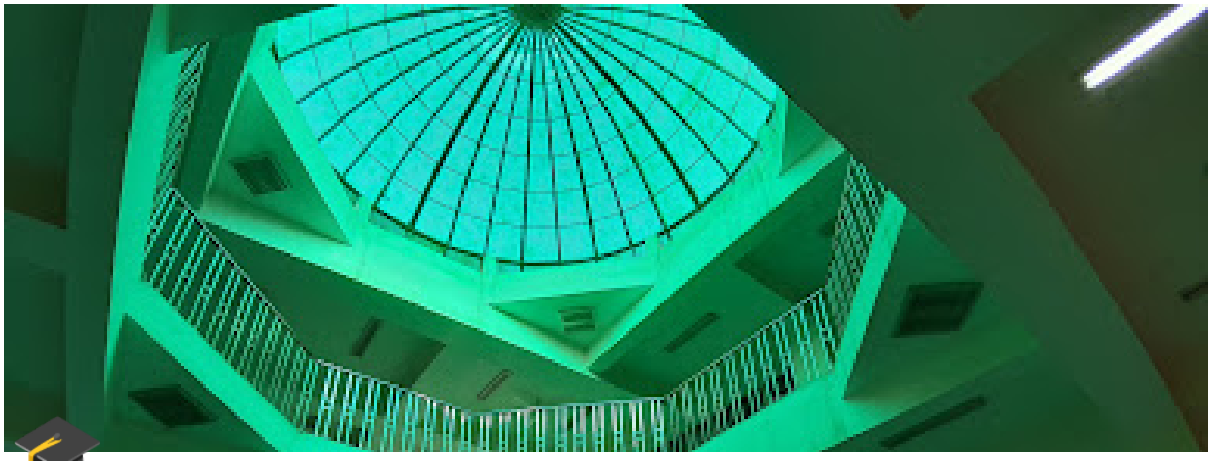

Notes | Atomic Structure | Unit 1 | Sessional Exam | B.Sc 1st Year | Chemistry (Major) | AMU |

Status	In progress
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Chapter	Structure of Atom
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Idea of de Broglie matter wave

- In 1924, Louis de Broglie proposed a new speculative hypothesis that electrons and other particles of matter can behave like waves.
- Every particle has a wavelength associated with it and relates the wavelength of that particle with its momentum.
- His work is known as the De-Broglie hypothesis of **matter wave.**
- He states that a light has both particles as well as **wave nature.**
- He derived the **relation between momentum and wavelength** of light using Einstein's special theory of relativity & Planks theory of wave.

> Einstein's special theory of relativity(i.e Einstein suggested that the light is made up of small packets called quanta or photons. Hence if light is a particle, it must have energy associated with it, given by:

$$E = mc^2$$

> Plank's Theory:If light is wave, its energy is given by:

$$E = hc/\lambda$$

de Broglie relation :As the both energy of wave and particle same,we have

$$mc^2 = \frac{hc}{\lambda}$$

$$\text{Or } \lambda = \frac{h}{mc}$$

$$\text{And } m \times c = p, i.e\ momentum\ of\ particle.$$

$$\text{Hence } \lambda = \frac{h}{p}$$

Heisenberg Uncertainity Principle

- The dual nature of the electron means that any precise measurement of its position would create some uncertainty in the measurement of its momentum and vice versa. This was pointed out by Werner Heisenberg in his Uncertainty Principles.
- According to this principle :
  ”It is impossible to determine exactly both the position and the momentum (or velocity) of an electron or of any other moving particle at the same time.”
- It means that when an electron behaves as a particle, its position can be determined more or less exactly but at the same time there would be uncertainty about its momentum or velocity.
- Similarly if the velocity or momentum can be determined precisely there would be uncertainty about its position.
- The uncertainty arises from the fact that when a measurement is carried out,the electron under investigation is to be viewed with a sensitive instrument such as a microscope, and in this process the light particles interact with the electron and alter its motion (i.e, velocity). It is not possible, therefore, say as to what the velocity of this electron is.
- **Uncertainity Equation:** If △x and △p are the uncertainities (i.e. error) in the measurement of position and momentum respectively of a particle , then :

$$\triangle x \times \triangle p > or = h/2\ \pi$$

- From this relation it is evident that when △x is small (i.e. the position of the electron is measured with accuracy), △p will be large(i.e. the momentum will be measured with less accuracy) and vice versa. In other words it means that the certaifity of determination of one property introduces uncertainty. for the determination of the other.
- If △E is the uncertainty in energy of thie particle and △T is the uncertainty in its time of passage past a particular point, then an equivalent relation illustrating the uncertainty principle would be :

$$\triangle E \times \triangle T > \frac{h}{2\pi}$$

Atomic Orbital

- Atomic orbital is defined as a three-dimensional region (or space) round the nucleus where there is higher prohability of finding an electron of specific energy.
- Here it should be noted that an **orbital** is a three-dimensional region within which there is a higher probability that ar electron having a certain energy will be found. On the other hand an **orbit** is two dimension.
- The best we can do is that we can only state or predict the probahility of locating (or finding) an electron with a probable velocity with particular energy'in a given region of space at a given time.
- Thus the uncertainty principle which is based on the wave-nature of the electron only gives the probability of finding an electron in a given space in place of certainty.
- It is for this reason that the old classical concept of Bohr has now been discarded in favour of the probability approach.
- The square ofΨ (i.e. Ψ^2) gives the probability of finding an electron of given energy in a given region round the nucleus. It is thus Ψ to identify regions of space round the ‘nucleus where there is higher probability of finding an electron having **definite amount of energy**. This space is called an atomic orbital. Thus :
- There is only one orbital in K shell with n=1. This orbital is called 1s orbital. In L shell with n=2 there are four orbitals viz. one 2s and three 2p (designated as 2p,, 2p, and 2p,) orbitals. Three 2p orbitals represent different oriegtations in space, Total number of orbitals in main shells are given below :

$K \rightarrow 1s$, $L \rightarrow 2s$, $2p_x$, $2p_y$, $2p_z$; $M \rightarrow 3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{z^2}$, $3d_{x^2-y^2}$; $N \rightarrow$ one $4s$, three $4p$, five $4d$ and seven $4f$ orbitals.

- **Representation of an orbital**: Although it is difficult to give a pictorial representation of an orbital, it is generally represented by a shaded figure in which the intensity of shading (shown by dots) is proportional to the probability of finding the electron at that location.

Fig. 1·9. Representation of probability of finding an electron in 1*s* orbital of hydrogen atom near the nucleus–electron cloud representation in hydrogen atom

- Fig 1.9 illustrates the probability of finding the electron in 1s orbital in hydrogen atom at certain positions near the nucleus.In this figure the density of dots is proportional to the probability of finding the electron at that location. It should be noted that this figure represents a two-dimensional cross-section of three-dimensional distribution of probability about the nucleus.
- This representation is of **electron cloud.**

SCHRODINGER WAVE EQUATION

- The fundamental wave equation describing the behaviour of a small particle in terms of wave motion is:

Basic understanding : (skip if you already know)

- **Wave Function :** A wave function in quantum mechanics is a description of the **quantum state** of a system.
- wave function is quantum state of any object how it behaves in a system.
- The value of the wave function of a particle at a given point of space and time is related to the likelihood of the particle's being there at the time.
- wave function represented by Ψ.
- A given point in space (identified by x, y, and z coordinates).
- A wave function, refers to a mathematical description of a particle's quantum state as a function of spin, time, momentum, and position.
- Typically the wave function obeys a **wave equation**.
- The most well-known example of such a wave equation is the Schrödinger equation.
- Since Ψ(x,t) is analogous to Amplitude of wave.

> For any kind of wave, we know Intensity is directly proportional to A^2.Here the Intensity means frequently observing the particle in a particular place. In other

words, Probability of finding the particle in a particular place . →Properties

- Quantum mechanics, as developed by Erwin Schrodinger in 1926, is based on the wave motion associated with the particles.
- For the wave motion of the electron in the three dimensional space around the nucleus, he put forward an equation, known after his name as Schrodinger wave equation, which is considered as the heart of quantum mechanics.
- The equation is :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

- where Ψ is the amplitude of the wave where the coordinates of the electron are (x, y, z), E is the total energy of the electron, V is its potential energy, m is the mass of the electron and h is Planck's constant. $d^2\Psi/dx$ represents second derivative of Ψ with respect to x and so on.
- In short, Schrodinger wave equation is written as $\hat{H}\Psi = E\Psi$ where $\hat{H}$ is a mathematical operator, called Hamiltonian operator
- The solution of Schrodinger wave equation for an electron in an atom gives the values of E and Ψ. The values of E represent the quantized values of energy which the electrons in the atom can have the corresponding values of Ψ are called wave functions.

Significance of Ψ and Ψ²

- The wave function Ψ by itself has no physical significance.
- However, its square (i.e.Ψ² *) measures the probability of finding ah electron of given energy from place to place in a given region round the nucleus, since the, probability of finding an electron in a-given region is proportional to* Ψ² i.e **electron density** at that point.
- Since the region around the nucleus which represents the electron density at different points is called an orbital, that is why the wave function for an electron in an atom is called **orbital wave function** or simply atomic orbital.

Quantum numbers

- Thesc quantum numbers arc the identification numbers for an individual electron in an atom, since these fully describe the position and energy of an electron in an atom.
- We have seen that Bohr''s Theory couid not explain the existence of fine structuré in the H-spectrum. The appearance of several lines in the H-spectrum, thercfore, indicates that only one quantum

number, n, suggested by Bohr, is not sufficient for specifying the various lines. There is now clear evidence in favour of the fact that four quantum numbers are needed to explain the various spectra.

1. Principal Quantum Number (n)

- This quantum number denotes the energy levél or the principal shell to which an electron belongs.
- It gives us info about the size and energy about an orbital.
- It is denoted by n.
- **Permitted values of n**: It can have only integral value from 1 to infinity, but 1 to 7 have so far been established. The letters K, L, M....are also used to designate the values of n. These letters stand to show the major energy level and correspond to n=1, 2, 3.....respectively.
- Thus when n=1,2, 3, 4..., the letter designations used are K, L, M, N, ... respectively.
- If for an electron n=3, it resides in the M-shell. n gives an idea of the size of the shell and is the same integral as suggested by Bohr in

$$mvr = nh/2\pi$$

2. Azimuthal Quantum Number (l)

- This quantum number is denoted by letter l .
- It gives info about shape of the orbital.
- It is also called angulor momentum quantum number, orbital quantum number and sometimes subsidiary quantum number.
- This quantum number was introduced by Sommerfeld in his atomic model and gives the angular momentum of the electron in its “precessional” elliptical movement round the nucleus and accounts for the fine structute inthe H-spectrum.
- Itgives an idea of the shape of the orbital.
- **Permitted values of /for a given value of n** : l can have any value from 0 to (n—1) for a given value of n i.e.

  l=0, 1, 2, ... (n-2), (n-1).
- The total numbes of different values of l is equal n . Thus, if n=1, l=0 {Only one value), n=2,l=0, 1 (Two values), n=3, l=0, 1, 2 (Three values), n=4, I=0, 1, 2, 3 (Four values).
- Tolal values of I for a given value of n gives the total number of sub-shells into which a main shell (.. K, L, M...) is divided, e.g. only one value of l (viz. 1=0) for n=1 (K-shell) shows that there is only one energy state in K-shell which is repicsented as (1 0) or 1s state. In 1s designation the number 1 stands for the valuc of n and the latter s denotes l=0. Similarly l=0, 1 for n=2 (L-shell) indicates that L-shell is divided into two sub-shells which are designated as (2 0) or 2s and (2 1) or 2p.
- Different values of I=0, 1, 2, 3,... are symbolised by the letters s,p,d, f... These letters designate the old spectral terms : sharp, principal, diffuse and fundamental respectively.

3.Explanation of Zeeman Effect and the Magnetic Quantum Number (m).

- We have already seen that Bohr could not explain the splitting of a single spectral line into a number of closely spaced lines in presence of a magnetic field (Zeeman Effeét) or in presence of electric field (Stark Effect).
- It gives us info about the orientation of the orbital.
- Aocording to Linde, the presence of more lines in the spectrum in a magnetic field or in an electric field indicates that the energy levels are further . sub-divided by the field and an additional quantum number, which he called magnetic quaritum namber, m, is needed to specify these energy sub-levels.
- Linde postulated that the electron producing the original line has in a magnetic field several possible space orientations for the same angular momentum vector (i.e., for the same value of /).
- Thus m is the quantum number corresponding to the component of the orbilal angular momentum along a reference direction for a single electron.
- **Permitted value of m :** For a given value of n, l takes the value 0 to n-1 an d for a given value of l, m takes the value -l to +l.

The magnetic and spin quantum numbers tell us about the **orientation of the electron**; they have to do with how the wave function changes under rotations.

4. Spin Quantum Number (s).

- This shows the spin of an electron in the orbital.
- When spectral lines of H, Li, Na and K ect were observed by means of the instruments of high resolving power, each line of the spectral series was found consisting of a pair of lines (known as doublets or double-line structure). Here it should be understood clearly that this doublet is diffcrent from fine structure which consists of closely-spaced fine lines (not widely- separated ones).
- To account for these doublets Uhlenbeck and Goud-Smith (1925) suggested that the electron, while moving round the nucleus in an orbit, also rotates (or spins) about its own -axis either in a clock- wise direction or in an anti-clockwise direction and this spinning of the electron about its own axis adds to the angular momentum of the electron i.e, the angular momentum of the electron is not only due to the motion of the electron round the nucleus but also due to the spinning of the electron.
- Acoordingly, the angular momentum of the clectron under this condition is. called spin angular momentum
  and is equal to

$$\sqrt{S(s+1)} \cdot \frac{h}{2\pi}$$

- where s stands for the absolute value of spin quantum number i.e. without sign.
- **Permitted values of s :** s can have two values viz +1/2 (corresponding to the spinning of the electron in the clock-wise direction) and -1/2(corresponding to the spinning in anti-clock-wise

direction).

- Clock-wise and anti-clockwise spinnings are represented as ↑ and ↓ respectively.
- Two clectrons with the same sign of spin quantum numbers are said to have parallel spins (shown as ↑ ↑), while those having opposite signs of spin quantum numberd are said to have opposite spins or anti-parallel spins (↑ ↓).
- Two electrons having opposite spins are said to be paired up electrons. .

Radial and angular wave functions

Wave function:

Basic understanding : (skip if you already know)

- **Wave Function :** A wave function in quantum mechanics is a description of the **quantum state** of a system.
- wave function is quantum state of any object how it behaves in a system.
- The value of the wave function of a particle at a given point of space and time is related to the likelihood of the particle's being there at the time.
- wave function represented by Ψ.
- A given point in space (identified by x, y, and z coordinates).
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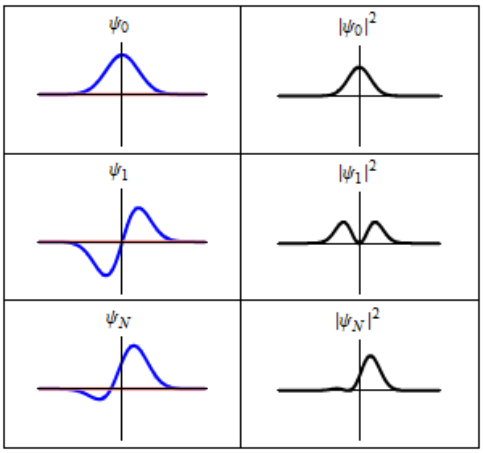
- Typically the wave function obeys a **wave equation**.
- The most well-known example of such a wave equation is the Schrödinger equation.
- Since Ψ(x,t) is analogous to Amplitude of wave.

> For any kind of wave, we know Intensity is directly proportional to A^2.Here the Intensity means frequently observing the particle in a particular place. In other words, Probability of finding the particle in a particular place . →Properties

- **Properties of Wave Function :**



1 Ψ must be continuous and single-valued everywhere.
2 $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
3 Ψ must be normalizable, which means that Ψ must go to 0 as $x \to \pm\infty$, $y \to \pm\infty$, $z \to \pm\infty$ in order that $\int|\Psi|^2\, dV$ over all space be a finite constant.

Radial wave function:

- Radial wave functions for a given atom depend only upon the distance, r from the nucleus.
- The radial wave function is the part that only depends on the radial coordinate r, not on the angular coordinates θ and ϕ .
- Angular wave functions depend only upon direction, and, in effect, describe the shape of an orbital

▼ Why does the radial wave function depend on principle and the azimuthal quantum number instead of the magnetic and spin quantum number?

If we rotate our coordinate system, the magnetic and spin quantum numbers can change, but the radial coordinate stays the same, so the radial wave function must be unchanged. So the radial wave function, which doesn't change under rotations, can't depend on the magnetic and spin quantum numbers, which can change.

▼ What does radial wave function depend on?

The radial part of the wave function depends on the principle quantum number (n) and azimuthal quantum number (l).

Angular wave function

- Angular wave functions depend only upon direction, and, in effect, describe the shape of an orbital.
- Depends on angular coordinates θ and ϕ .
- Angular wave function also depend on magnetic and spin quantum number.
- The angular wave functions for a hydrogen atom, Yl,ml(θ,ϕ) are also the wavefunction solutions to Schrödinger's equation for a rigid rotor consisting of two bodies, for example a diatomic molecule.

Probability distribution curve

- In an atomic orbital there is a probability of findig the electron in a particular region at a given radial distance and in a particular direction from the nucleus. This give rise to two types of probability of finding electron:

1. Radial probability distribution curve
2. Angular probability distribution curve

Radial probability distribution curve

- These curves give the probability of finding an electron in a given atom upon the distance, r from the nucleus.

Angular probability distribution curve (shapes or boundary surfaces of orbitals)

- These curves give the probability of finding an electron in any given direction from the nucleus without reference to
  its distance from the nucleus.

Shapes of s,p,d orbitals

Shape of s-orbitals

- We have seen that for s-orbitals l=0. For l=0,m=0 which indicates that s-orbitals have only one orientation.
- Since for all s-orbitals there is only one orientation, these are spherically symmetrical,
- i.e.electron density in s-orbitals is not concentrated along any particular direction.
- There is an equal chance of finding the electron density in any direction with respect to the nucleus (see Fig. 1-12).

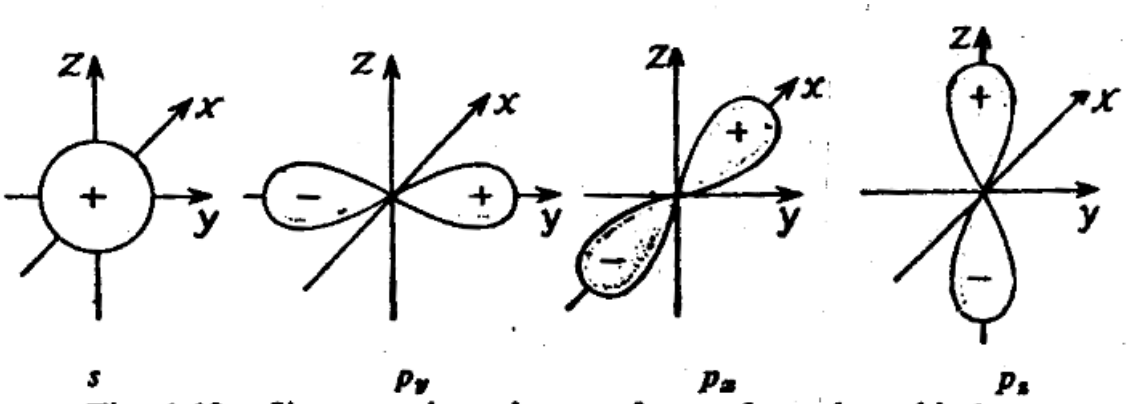


Fig. 1·12. Shapes or boundary surfaces of *s* and *p*-orbitals, *yz*, *xz* and *xy* are the nodal planes of p_x, p_y and p_z orbitals.

Shape of p Orbitals

- Each p orbital consists of two sections better known as lobes which lie on either side of the plane passing through the nucleus.
- The three p orbitals differ in the way the lobes are oriented whereas they are identical in terms of size, shape, and energy.
- As the lobes lie along one of the x, y or z-axis, these three orbitals are given the designations 2px, 2py, and 2pz. Thus, we can say that there are three p orbitals whose axes are mutually perpendicular.
- Similar to s orbitals the size, and energy of p orbitals increase with an increase in the principal quantum number (4p > 3p > 2p).

Shape of d-orbitals

For d-subshell, *l* = 2, there are five values of m namely -2, -1, 0, 1, 2. It

means d- orbitals can have five orientations. These are represented by dxy, dyz,

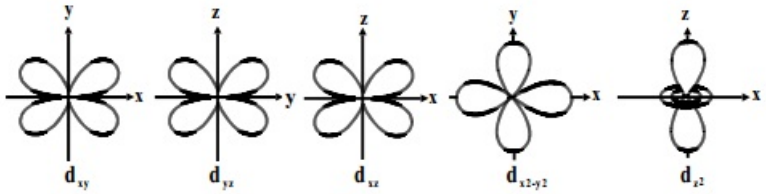


Fig. Shapes of d-orbitals

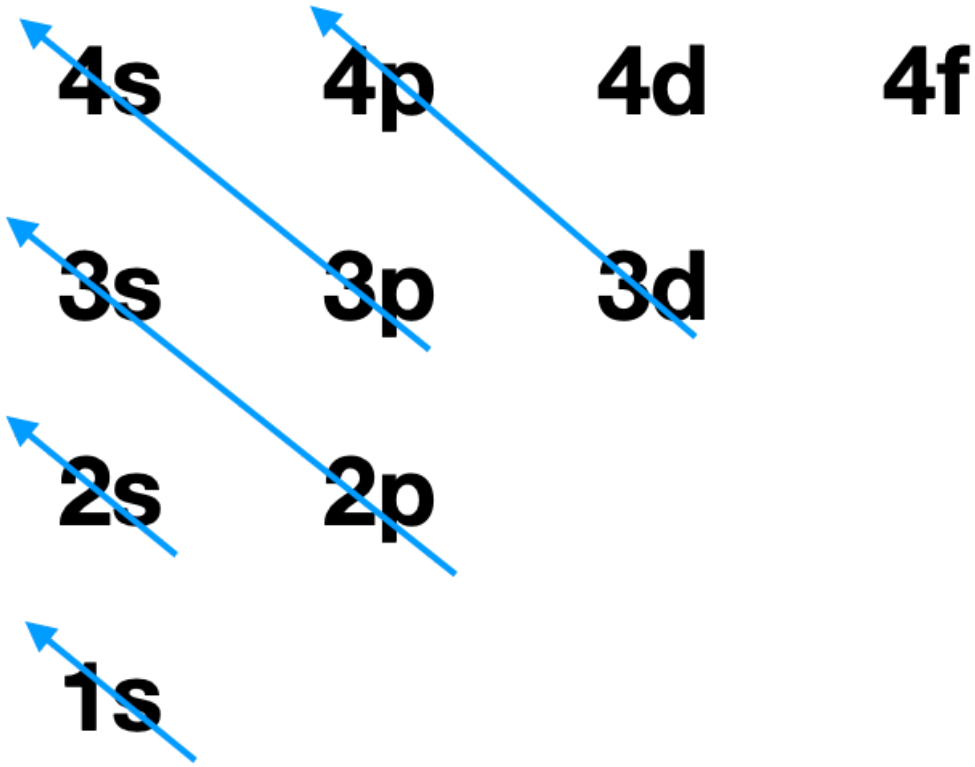
dzx, dx2-y2 and dz2; for example, 3dxy, 3dyz, 3dzx, 3dx2-y2 and 3dz2. The dxy, dyz and dzx orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZX-

planes respectively.The dz2 orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the centre. The dx2-y2 orbital is also clovar leaf shaped but its leaves are directed along the X and Y- axis.

The reason for the presence of four lobes in any nd orbital lies in the fact that the d - orbitals have two nodes, and hence two changes in algebraic sign of ψ, which lead to four lobes.

Aufbau Principle

Electrons will occupy the lowest energy orbitals in order to minimize the total energy.



Hund's rule of maximum multiplicity

A simplified definition of Hund's rule is that **the lowest energy arrangement is the one with the greatest number of unpaired electrons**

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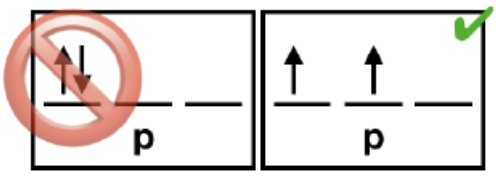
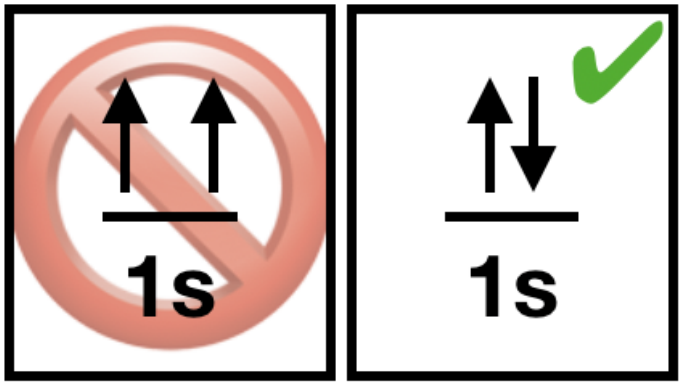


# of electrons in a p-subshell	Arrangement (unpaired electrons, n)	Spin Multiplicity (n + 1)
1	(n = 1)	2
2	(n = 2)	3
3	(n = 3)	4
4	(n = 2)	3
5	(n = 1)	2
6	(n = 0)	1

The Pauli exclusion principle

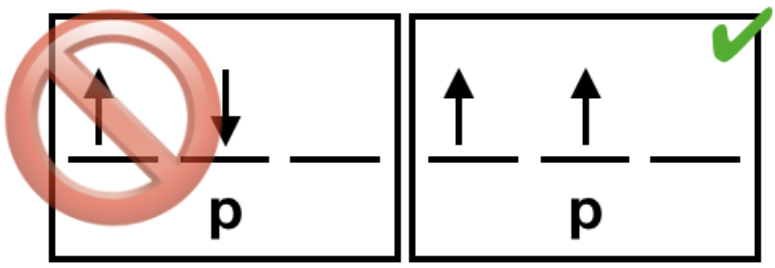
states that it is impossible for two electrons of a multi-electron atom to have the same set of values for all four quantum numbers.



The exchange interaction

The exchange interaction results in a ground state electron configuration with unpaired electrons all being of the same spin.

it is a quantum mechanical effect that takes place between identical particles.



Guess the place in the cover:

Hint: The largest university library in Asia